PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Curing of Polymeric Materials.

We, DAVID AUGUSTINE HARPER and WALTER FAIRBAIRN SMITH, both of Hexagon House, Blackley, Manchester, British Subjects, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a Company incorporated under the laws of Great Britain, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the curing of polymeric materials more especially to the curing of organic diisocyanate modified poly-esteramides in admixture with other polymeric materials.

In Application numbered 13204/41 (Serial No 580,524) it has been proposed to cure organic diisocyanate modified polyester-amides by heating these in the presence of formaldehyde or of a formaldehyde-liberating substance, and preferably, also in the presence of materials which function as curing catalysts, for example, formic, glycollic, oxalic, succinic, maleic, adipic, tartaric, salicylic, anthranilic, phthalic, citric, boric and phosphoric acids, phthalic and maleic anhydrides, phthalimide and potassium or sodium dihydrogen phosphate.

In Application numbered 7392/42 (Serial No. 580,526) it has been proposed to cure organic diisocyanate modified polyester-amides by heating these in the presence of formaldehyde or of a formaldehyde-liberating substance and also in the presence of curing catalysts which are substantially neutral but which develop acidity only under curing conditions, for example butadiene sulphone, 2:3-dimethylbutadiene sulphone, butadiene tetrabromide, styrenedibromide, acetylene tetrabromide, tribromohydroquinone, 1-bromo-2 naphthol, 1:6-dibromo-2-naphthol, 1:4:6-tribromo-2-naphthol, 2:4-dibromo-1-naphthol, methyl-α:β-dibromopropionate, β-chloroethyl-α:β-dibromoisobutyrate, ethyl α-bromo-propionate, phenyl trichloroacetate, α:α:β trichloropropionitrile, trichloroacetamide, trichloroacetyldiethylamide, N-trichloroacetylanilide, N:N¹-di(trichloroacetyl) methylenediamine, N:N¹-di-(trichloroacetyl)ethylenediamine, interpolymers of asymmetrical dichloroethylene and vinyl chloride, and chloranil tetrachloro-*p*-benzoquinone).

In Application numbered 10290/43 (Serial No. 581,146) it has been proposed to use dichromates for curing organic diisocyanate modified polyester-amides.

We have now found that the organic diisocyanate modified polyester-amides may be cured, with advantage, together with small or large proportions of other polymeric materials which are themselves reactive to formaldehyde and/or dichromates.

According to the present invention in the curing of organic diisocyanate modified polyester-amides in the manner hereinafter set forth we provide the improvement which comprises curing said modified polyester-amides in uniform admixture with a proportion of a derivative of cellulose.

The invention also comprises heat-curable compositions comprising as the essential ingredients an organic diisocyanate modified polyester-amide, a proportion of a derivative of cellulose, and one or more materials of the kind hereinafter set forth such as are customarily used for curing organic diisocyanate modified polyester-amides.

Water-soluble or water-insoluble derivatives of cellulose include cellulose esters, for example, cellulose nitrate and cellulose acetate, and cellulose ethers such as benzyl cellulose. These materials are modified by the action of formaldehyde thereon, and they are compatible with the organic diisocyanate modified polyester-amides, in the sense that they are capable of forming homogeneous blends therewith.

The derivative of cellulose may be brought into uniform admixture with the organic diisocyanate modified polyester-amide in several ways. For instance, a derivative of cellulose dissolved in water is slowly added to an organic diisocyanate modified polyester-amide running on a warm rubber mill. Or, a derivative of cellulose in powder form, is milled into an

organic diisocyanate modified polyester-amide on a rubber mill, a sufficiency of water usually being added to render the mix soft. When water is used before or during the incorporation, the mix is usually milled until it is substantially dry, the rolls, if hot, being preferably allowed to cool during the drying so as to minimise the risk of the mix sticking thereto. Alternatively, the components are mixed or milled together (in the absence of water) as such or in the presence of organic liquids which are solvents for one or more of the materials; the organic liquids are removed as and when convenient.

The proportions of the components are not critical, but usually from about 25 to 175 parts of the derivative of cellulose per 100 parts of organic diisocyanate modified polyester-amide are used.

The mixtures are cured by means of any of the materials customarily used for curing organic diisocyanate modified polyester-amides, that is to say, by heating with a known curing agent, namely, formaldehyde or a formaldehyde-liberating substance or a dichromate, preferably in the presence of a known curing catalyst, namely, an acid or a material which is substantially neutral but which develops acidity under curing conditions. These ingredients required for curing are incorporated with the mix whenever convenient but, if water has been used to assist in the formulation of the mix, preferably after the mix is dried.

As well as those already mentioned, one or more additional compounding ingredients may also be used. These include fillers, for example, carbon black, iron oxide, clay, asbestos, blanc fixe, whiting, lithopone and mica; resins, for example, urea-formaldehyde and phenol-formaldehyde resins; other plastic materials, for example, natural or synthetic rubbers, vulcanised vegetable oils, dark substitute, white substitute, a Cumar resin, wood rosin and pitch; de-tackifying agents, that is to say, materials which reduce the tendency of the mix to stick to the rolls, for example, stearic acid, paraffin wax, oleic acid, lauric acid and dibutyl ammonium oleate; plasticisers, for example tricresyl phosphate, dibutyl phthalate, butylphthalyl butyl glycollate, and N-alkyl-toluenesulphonamides; stabilisers or anti-oxidants, for example, hydroquinone, N:N¹-hexamethylene-bis-ortho-hydroxy-benzamide, N-phenyl-α-naphthylamine, N-phenyl-β-naphthylamine and α:α-bis(2-hydroxy-3:5-dimethylphenyl)butane, as well as others commonly used in rubber technology. Small quantities of pigments, for example from 1—3% by weight, such as are customarily used in rubber technology or in the coating composition art may also be used to impart colour. The use of alkaline reacting compounding ingredients should be avoided since these may cause degradation of the polymeric materials.

When the ingredients are mixed, the mix is removed from the mill or mixer, if desired, formed into shapes or spread or calendered on to a substrate, for example on to the surface of a fabric, or on to the surface of a coated fabric and then curing is effected by heating, for example, in a mould which is preferably in a hydraulic press, or in hot air. Periods of heating varying from a few minutes to several hours at 100—150° C. are usual. If desired, to facilitate shaping or spreading, organic solvents or swelling agents or additional solvents or swelling agents may be incorporated with the materials; these are removed as and when convenient.

Suitable organic solvents include acetone, mixtures of benzene and acetone, mixtures of benzene and ethanol, mixtures of benzene and chloroform, mixtures of benzene and methylethyl ketone, mixtures of methyl ethyl ketone and trichlorethylene, and mixtures of acetone and the monoethyl ether of ethylene glycol.

Polyester- and polyamide-forming reactants suitable for making the diisocyanate modified polyester-amides to be used for the purposes of the present invention include glycols, for example, ethylene glycol, diethylene glycol, trimethylene glycol, pentamethylene glycol, hexamethylene glycol, dodecamethylene glycol, 1:12-octadecanediol and pentaglycol; aliphatic or aromatic amino-alcohols having at least one hydrogen atom attached to the amino nitrogen atom and preferably containing an aliphatic chain of at least two carbon atoms separating the amino and hydroxyl groups, for example β-ethanolamine and 3-amino-propanol; dibasic carboxylic acids or ester-forming derivatives thereof, preferably aliphatic dicarboxylic acids, for example, malonic, succinic, glutaric, adipic, β-methyladipic, pimelic, suberic, azelaic, sebacic, undecanedioic, brassylic, *iso*-phthalic, hexahydroterephthalic, *p*-phenylenediacetic, and acetone-dicarboxylic acids; primary and secondary diamines, for example, ethylene diamine, hexamethylenediamine, 3-methylhexamethylene diamine, decamethylenediamine, *m*-phenylenediamine, N:N¹-dimethylhexamethylenediamine, N:N¹-diethylhexamethylenediamine, and N:N¹-dimethyldecamethylenediamine; monohydroxymonocarboxylic acids or their ester-forming derivatives, for example,

glycollic, 6-hydroxycaproic, 10-hydroxydecanoic and 12-hydroxystearic acids; polymerizable monoaminomonocarboxylic acids, or their ester-forming derivatives, for example, 6-aminocaproic acid or its lactam, caprolactam, and 9-aminononanoic, 11-aminoundecanoic and 12-aminostearic acids.

The polyester-amides are made in known manner by heating the selected reactants at polymerizing temperatures, usually in the absence of air or oxygen, under conditions whereby water is removed from the reaction mixture. When a diamine is to be used, it is conveniently used in the form of the corresponding diammonium salt from some of the dibasic carboxylic acid to be used.

The polyester-amides are modified with organic diisocyanates in known manner for example, by mixing them, for example by stirring, milling or kneading, with the organic diisocyanate and then heating the mixture, for example, to a temperature of 100—200° C. for a period of 10—720 minutes. Up to about 10 per cent., usually 3—7%, by weight of the diisocyanate is used.

Examples of organic diisocyanates includes ethylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate decamethylene diisocyanate, *p*-phenylene diisocyanate, *m*-phenylene diisocyanate, $p:p^1$-diphenyl diisocyanate, diphenylmethane-$4:4^1$-diisocyanate, naphthalene diisocyanates and adipyl diisocyanate.

The new heat-curable compositions of the invention may be used in the fabrication of a variety of articles, in which they may or may not be supported on a substrate and/or interspersed with fillers. For instance, they may be used in the construction of organic liquid resistant articles of all kinds, for example, gaskets, packings, hose, diaphragms for pumps and the like, as well as in the fabrication of flexible containers. They may also be used in the coating of rollers, blankets and stereos for use in the printing industry, or to provide protective sheathings for insulated electric cables and other electrical conductors. They also find application in the coating of the balls for games, tyres and flexible materials generally, including fabrics, protective clothing, leather cloth and floor coverings, and generally in the construction of articles requiring the use of a material having physical properties resembling those of rubber, but also having a good resistance to the action of organic fluids and a low permeability to gases and vapours.

They are well adapted for application in the form of lacquers or finishing compositions for all kinds of surfaces. They may be formed into films or sheets, for example, as substitutes for leather or as wrapping films, and they may be used as adhesives for a wide variety of materials, for example, wood, metals, fabrics, paper, leather and regenerated cellulose.

The invention is illustrated but not limited by the following Examples, in which the parts and percentages are expressed by weight, unless otherwise stated:—

EXAMPLE 1.

Into 100 parts of an organic diisocyanate modified polyester-amide there are milled 10 parts of titanium dioxide, 5.0 parts of hexamethylolmelamine hexamethyl ether and 0.75 parts of 2:4-dichloro-1-naphthol. The mix is then let down in 100 parts of a mixture of equal volumes of benzene and acetone, and 125 parts of a 20% solution of cellulose acetate (acetone-soluble) are stirred in. The mix is thinned with acetone to a solids content of 10—15% and is ready for use.

The composition is flowed on to a glass plate, the solvent is allowed to evaporate, and the so obtained film is cured by heating in air at 125° C. for 2 hours.

The cured film is tough and has a rubbery handle; its surface is very resistant to scratching.

When the recipe of the Example is repeated using twice the quantity of the solution of cellulose acetate, a film is obtained which is tougher, less rubbery, harder, and extremely resistant to scratching.

Similarly, when the recipe of the Example is repeated using three times the quantity of the solution of cellulose acetate, there is an increase of toughness and hardness, and a decrease of rubbery properties; the film has outstanding resistance to scratching.

EXAMPLE 2.

Into 100 parts of an organic diisocyanate modified polyester-amide there are milled 10 parts of titanium dioxide, 5.0 parts of hexamethylolmelamine hexamethyl ether and 0.75 parts of 2:4-dichloro-1-naphthol. The mix is let down in 100 parts of a mixture of equal volumes of benzene and acetone, and 250 parts of a 20% solution of nitrocellulose obtainable commercially under the name "Collodion Cotton HX 30/50" are stirred in. The mix is thinned with acetone to a solids content of 10—15% and is ready for use.

The composition is flowed on to a glass plate, the solvent is removed by evaporation, and the so obtained film is cured by heating in air at 125° C. for 2 hours.

The cured film is tough, rubbery and

has a very good scratch resistance.

When the recipe of the Example is repeated using half as much again of the nitrocellulose solution, a tougher, less rubbery film with better scratch resistance is obtained.

EXAMPLE 3.

A lacquer is prepared by mixing together 100 parts of an organic diisocyanate modified polyester-amide, 60 parts of the cellulose acetate used in Example 1, 10 parts of carbon black, 5 parts of hexamethylolmelamine hexamethyl ether, 0.75 parts of 2:4-dichlor-1-naphthol, 200 parts of ethylene glycol monoethyl ether and 350 parts of acetone.

The so obtained lacquer is used to provide a top-coating for the hydrolysed leather-organic diisocyanate modified polyester-amide coated fabric obtained in the manner set forth in Application numbered 21389/43. (Serial No. 583,862), and more specifically as follows:—

130 parts of disintegrated scrap vegetable-tanned leather are mixed with sufficient cold water to form an easily stirred slurry, the slurry is heated up to boiling and boiled for about 5 minutes. The leather settles in the form of a crumbly mass from which the liquid is poured off. The wet mass is added in small amounts to 100 parts of an organic diisocyanate modified polyester-amide running on to a rubber mill with the rolls heated to about 70° C.; the mix is milled until homogeneous, and then dried on the rolls. The following ingredients are then added in the order listed, 0.5 parts stearic acid, 30 parts of titanium dioxide, 5 parts of hexamethylolmelamine hexamethyl ether and 0.75 parts 2:4-dichloro-1-naphthol, milling is continued until the mix is again homogeneous, and it is then sheeted off the mill.

The sheet is added to its own weight of a benzene-ethanol mixture (75:25 by volume) in a Werner Pfleiderer mixer, and mixed until a smooth dough is obtained. The dough is spread on to a cotton twill fabric, the organic liquids are allowed to evaporate.

The coated spreading is then cured by heating in air at 125—130° C. for 2 hours.

The cured material has a high gloss, an excellent abrasion, scrub and flex resistance, and an outstanding resistance to scratching or marking.

The organic diisocyanate modified polyester-amide used in the above Examples is that described in Example 7 of Application numbered 13204/41 (Serial No. 580,524).

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. In the process of curing organic diisocyanate modified polyester-amides in the known manner hereinbefore set forth, the improvement which comprises curing said modified polyester-amides in uniform mixture with a proportion of a derivative of cellulose.

2. The improvement which comprises curing organic diisocyanate modified polyester-amides in uniform admixture with a proportion of a derivative of cellulose in the manner hereinbefore particularly described and ascertained especially with reference to the foregoing Examples.

3. Organic diisocyanate modified polyester-amides whenever cured in uniform admixture with a proportion of a derivative of cellulose according to either of the preceding claims.

4. Heat-curable compositions comprising as the essential ingredients an organic diisocyanate modified polyester-amide, a proportion of a derivative of cellulose, and one or more materials of the kind hereinbefore set forth such as are customarily used for curing organic diisocyanate modified polyester-amides.

Dated the 28th day of September, 1945.

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